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Persistence of fenitrothion residues in a conifer forest environment

K.M.S. Sundaram, R. Nott

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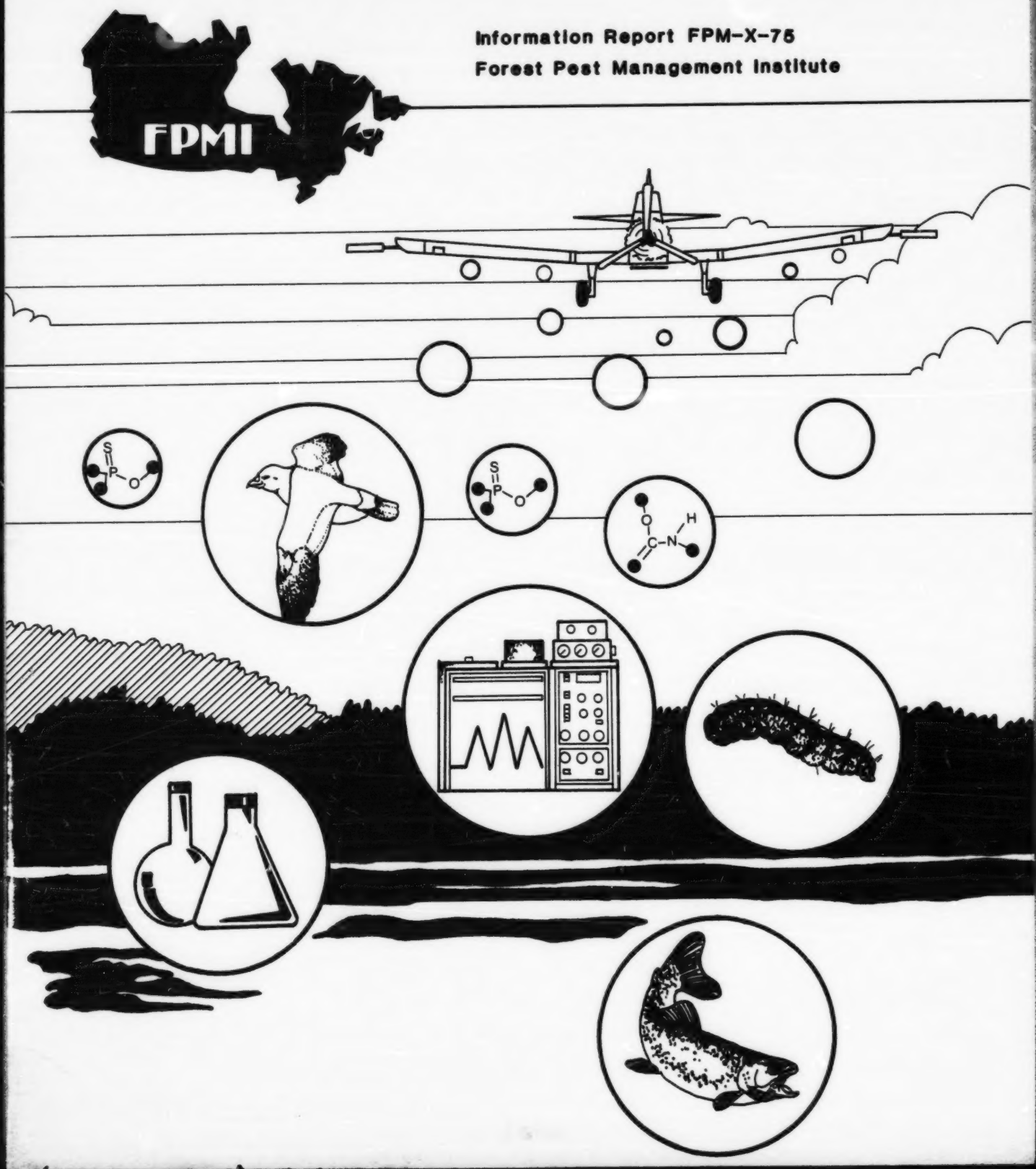

PERSISTENCE OF FENITROTHION RESIDUES IN A CONIFER FOREST ENVIRONMENT

INFORMATION REPORT FPM-X-75

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ABSTRACT

Persistence of aerially sprayed fenitrothion in various forestry substrates sampled from 8 plots in New Brunswick's forests were investigated. Following established sampling methods, air, water, sediment, aquatic plants, fish, balsam fir, *(Abies balsamea* [L.] Mill.), foliage, forest soil and litter samples were collected from unsprayed plots during the 1982 operational spray program in the province and again resampling them from the same plots a year later just prior to the commencement of operational spraying. Control samples were collected from an unsprayed site, near Sault Ste. Marie, Ontario. All samples collected during the two regimes and the control samples were carefully analysed for fenitrothion residues. The data collected were evaluated statistically. All the substrates, except fish, sampled during the operational spraying contained fenitrothion. Samples collected a year later, prior to any operational spray, did not contain any detectable levels (10 ng/m^3 for air, 0.01 ppb for water and 0.01 ppm for others) of the insecticide except the fir foliage. The findings confirmed that all 8 sampling plots received drift from nearby operational spray areas in 1982 and were contaminated. New and old fir needles sampled a year later from all 8 plots contained on average about 0.55 µg of the chemical (0.55 ppm) per gram of fresh foliage. The study conclusively proved that the conifer needles acted as a micro sink for the chemical and the latter has a tendency to persist in them.

RÉSUMÉ

La rémanence du fénitrothion épandu par voie aérienne a été étudiée dans divers substrats dans 8 placettes établies dans les forêts du Nouveau-Brunswick. Des échantillons de l'air, de l'eau, des sédiments, des plantes aquatiques, des poissons, du feuillage du sapin baumier *(Abies balsamea* [L.] Mill.), du sol de la forêt et de la litière y ont été prélevés, dans des placettes non arrosées durant le programme d'arrosages opérationnels en 1982; d'autres échantillons ont été prélevés dans les mêmes parcelles un an plus tard, juste avant le début des arrosages opérationnels. Des échantillons témoins ont été prélevés à un endroit non arrosé près de Sault Ste. Marie, en Ontario. Tous les échantillons recueillis ont été analysés minutieusement. Les données obtenues ont été évaluées selon des méthodes statistiques. Le fénitrothion a été décelé dans tous les substrats qui ont été échantillonnés au cours de l'arrosage opérationnel, saufle le poisson. Les échantillons recueillis un an plus tard n'en renfermaient pas en concentrations décelables (limites de détection: 10 ng/m^3 pour l'air, 0,01 ppb pour l'eau et 0,01 ppm pour les autres), sauf ceux du feuillage. Les résultats confirment que les huit placettes d'échantillonnage ont été touchées et contaminées à la suite des arrosages opérationnels effectués à proximité en 1982. Les nouvelles et vieilles aiguilles de sapin prélevées un an plus tard dans les 8 placettes renfermaient en moyenne environ 0,55 µg de l'insecticide (0,55 ppm) par gramme à l'état frais. Les résultats prouvent de façon concluante que les feuilles de conifères ont agi comme un micropiège pour le produit chimique et que celui-ci a tendance à persister chez elles.

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INTRODUCTION

Fenitrothion [0,0-dimethyl 0-(3-methyl-4-nitrophenyl) phosphorothioate] is a well established organophosphate insecticide that has been used extensively since 1963 in the control of spruce budworm, *Choristoneura fumiferana* (Clem.) in eastern Canada, especially in the provinces of New Brunswick and Quebec. It is usually applied by aircraft during the latter part of May to mid-June at dosages of 0.14 to 0.28 kg AI/ha to reduce damage by the insect pest. Up to the end of 1985, about 10×10^6 kg of the material had been released over 35×10^6 ha of conifer forest.

Fenitrothion has been extensively sprayed for the past many years over the forests of New Brunswick. Its lipophilicity, shown by the high octanol/water partition coefficient (K_{ow} = 2380 at 20°C), its environmental stability and low vapour pressure (183×10^{-4} Pa) have, to a certain extent, resulted in the chemical persisting in some components of the forest environment (Yule and Duffy 1972; Yule 1974; Sundaram 1974a, b; Sundaram, 1984b; Ayer *et al.*, 1984). Some of the earlier data reported on fenitrothion persistence in plots that received no direct spray application in the sampling year were gathered while operational spraying was being carried on in the surrounding area. Consequently indirect entry of the chemical *via* drift into the sampling sites has been a possibility (Pearce *et al.*, 1979; Mallet and Volpe, 1982; Sundaram 1984a). Therefore definitive information is still lacking on the residue component arising from persistence of the chemical influenced by its physicochemical properties coupled with replicate applications over the years and residue components contributed by drift from neighbouring spray areas. Recently Sundaram (1984b) and Ayer *et al.* (1984) addressed the persistence aspect of the chemical in their studies but a paucity of knowledge still exists on the contribution of drift from elsewhere in the year of sampling to the overall residue levels of fenitrothion found in certain forestry materials. This can be adequately discerned only if various forestry substrates are sampled initially for residue determination in unsprayed plots located far away from ones receiving operational applications, with resampling from the same plots a year later, just prior to the commencement of operational spraying. If residue levels found in the substrates collected from the plots following the two sampling regimes are compared, it should be possible to identify the contributions arising from drift to the overall persistence of the chemical in forestry substrates. This paper describes the first of such studies made in the forest areas of New Brunswick during the operational spray program of summer 1982 to evaluate the possible drift component and subsequently in the spring of 1983 just prior to any operational spraying to establish the persistence of the chemical due to its physical properties.

MATERIALS AND METHODS

Plot Selection

Eight plots, ranging in size from 50 to 4300 ha, were selected in the northern and southern parts of the province of New Brunswick. Three plots (P1, P2 and P3) were near Bathurst, three (P4, P5 and P6) were near Charlo and two (P7 and P8) were near Fredericton. The plots had been sprayed many times prior to 1982 with varying doses of fenitrothion, but received no direct application in 1982. The surrounding areas had similar spray histories and, in addition, they also received operational dosages of the chemical during the 1982 spray season. The sampling plots P1 to P8, the surrounding operational spray areas, and the dosages received during the 1982 spray season are shown in Figure 1. Information pertaining to various fenitrothion spray applications conducted by individual woodlot owners around the Fredericton area was not available. Some particulars of the plots, their locations and coordinates and the materials sampled from each are given in Table 1.

Sampling of Substrates

The first sampling regime was done in May/June of 1982 during the middle of the

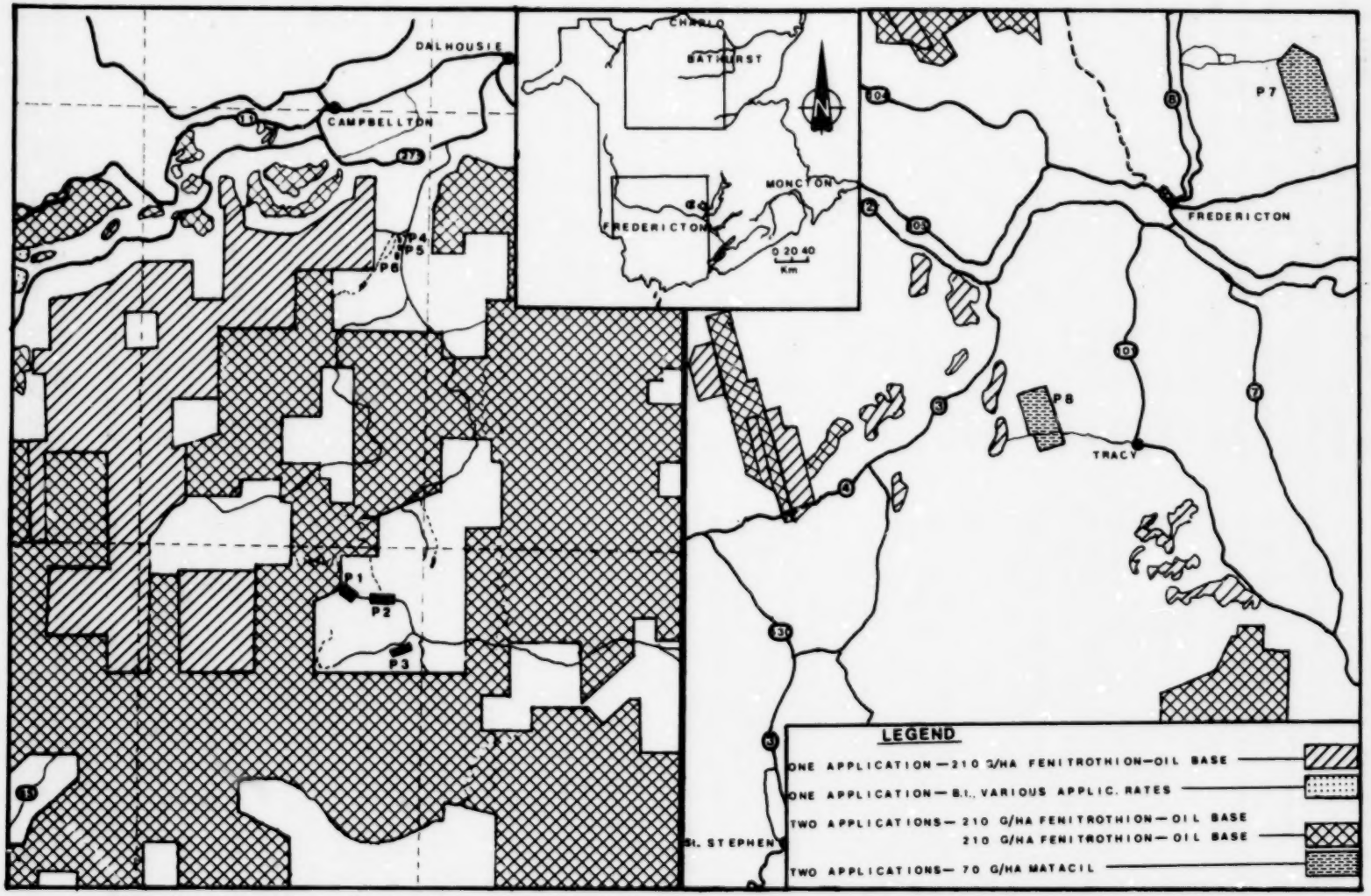

Fig. 1. Location of sampling plots used in the province of New Brunswick during the 1982/83 studies. (Inset: Province of New Brunswick showing the study areas.)

Table 1. Some particulars of the sampling sites used in the province of New Brunswick during 1982/83 study

Plot	Approx. area of each plot (ha)	Location (parish/county)	Coordinates	Substrates sampled
P1, P2 and P3	200	Northesk/Northumberland	47°24'N; 66°31'W	Air, water, sediment, moss, fish*, fir foliage, litter and soil
P4, P5 and P6	50	Balmoral/Restigouche	47°50'N; 66°30'W	Air, water, sediment, moss, fir foliage, litter and soil
P7	4300	St. Mary's/York	46°08'N; 66°49'W	Air, water, sediment, moss, fish, fir foliage, litter and soil
P8	3200	New Maryland/York	45°42'N; 66°49'W	Air, water, sediment, watercress, moss, fish, fir foliage, litter and soil

* Fish were found only in P1.

operational spray program in the province. The second monitoring program was done in the early part of May 1983 just prior to the commencement of any type of spray application.

The amount of persistent residues of fenitrothion in forestry substrates are expected to be low and most likely would be in the order of ppb (ng/g) levels (Sundaram, 1974a, b; Sundaram, 1984b; Ayer *et al.*, 1984). Therefore to achieve a meaningful and realistic picture of environmental persistence of the chemical and to relate properly the causative factors behind it, a rigorous fenitrothion monitoring program, based on the recommendations of U.S. Federal Working Group on Pest Management (1974) was adopted. The selection of the majority of substrates and the sampling techniques used to collect them were based on the recommendations of this expert group with necessary modifications introduced to suit the experimental conditions.

Sampling of water: Depending on accessibility, four equidistant sampling sites were established across the transverse section of each stream where the water flow was uniform with good mixing . From each site, the water was sampled by dipping a clean wide-mouthed open 1 L Teflon® bottle just about 1 cm beneath the water surface and allowing the water to flow in until about 75% of the bottle was filled without stirring up and entraining bottom sediment. The bottle was closed tightly with the Teflon screw cap, labeled and stored at 0°C in a cooler. Water samples were also collected from the ponds in plots P3 and P5 from four randomly selected sites, covering their horizontal cross sections. In the laboratory, prior to extraction, all four water samples from each stream or pond were pooled to form two composite subsamples. Similar quadruplicate samples were collected at each site of the other streams and were composited prior to extraction and analysis.

Sediment: Using the same sites in each stream and pond where the water was sampled, four scoops of sediment each weighing about 100 g were taken using a clean wide-mouthed amber coloured glass bottle fitted with Teflon -lined screw caps. At each sampling site, the bottle was gently lowered to the

bottom, the lid unscrewed and one single scoop of sediment of about 1 cm thick was taken. The bottle was tightly sealed, brought to the surface and decanted gently to remove all the inflowed water. All four sediment scoops collected from the four sites were pooled after removing all the debris to form a single composite sample. The samples were labeled, sealed and brought to the field laboratory in coolers at 0°C and kept frozen until analysis.

Moss (*Fontinalis dalecarlica*, Fontinalaceae) and water-cress (*Nasturtium officinal*, Cruciferae): Apart from plot P8, none of the streams contained water-cress. Moss was present in all except plot P4. Both types of sample were collected by scooping about 6 bunches per sample around the same vicinity where water samples were collected. The adsorbed water was squeezed out, and each sample was wrapped separately in aluminum foil, packed in a labeled polyethylene bag, chilled immediately and transported to the field laboratory for storage at -10°C.

Fish: Brook trout, *Salvelinus fontinalis*, was the predominant resident fish species in the streams in P1, P7 and P8 and served as the indicator species in the present study. The streams in the other plots were too shallow to contain any species of fish. Three to five uniform sized fish (mean wt 10 ± 5 g and mean length 8 ± 4 cm) contributing to a composite sample per sampling station were collected either by hook and line or by electroshocking in the same area where water and sediment were sampled. Each composite sample was wrapped in aluminum foil, packed in a labeled polyethylene bag and chilled immediately prior to transport to the field laboratory where they were stored at -10°C until analysis. During analysis, the whole fish in a composite sample was analyzed after homogenization.

Air: Six sampling sites covering an area of about 5 ha in each plot were selected after considering prevailing wind speed and direction, canopy density, topography, etc. The air at each site was sucked in continuously at constant speed (0.5 L/min) for 60 min, as described earlier (Sundaram, 1984a), by battery operated pumps into glass impingers containing toluene as the trapping medium. The flow rate of each air sampler was carefully calibrated each time prior to use to determine exactly the volume of air sampled during the 60 min sampling period. The sampler and the collecting reagent were pretested earlier in the laboratory using fenitrothion vapour for sampling efficiency and retention at the planned air flow rate in the field. The collecting reagents from the samplers were pooled to get three composite samples per plot and they were stored in clean screw top amber coloured glass containers with aluminum foil liners and refrigerated.

Litter: Twenty sampling sites covering an area of approximately 10 ha were selected randomly in each plot. One uniform core (diam. 5.0 cm, depth 4.0 cm), was collected per site with a tube sampler to account for the variation present within the plot. The tube sampler was cleaned after sampling each plot by scrubbing it with a brush and water then rinsing with acetone. The roots, twigs, stones and other undecomposed organic debris were removed, the 20 individual cores were composited, packed in labeled plastic bags, mixed thoroughly, transported to the field laboratory in a cooler at 0°C and stored in a freezer. Prior to analysis, the composited litter was macerated in a Hobart food chopper and passed through a 10-mesh sieve (2 mm openings) and aliquot quantities were used in the analysis.

Soil: Twenty sampling sites without any litter or grass cover, containing primarily mineral soil were selected in the vicinity, where litter samples were collected. Sampling and processing of the collected materials were done as described under litter.

Balsam fir foliage: Ten dominant fir [*Abies balsamea* (L.) Mill] trees (approximately 15 m in height and 15 cm DBH) with developed crowns, ample growing space and exposure to sunlight were selected randomly from an area covering nearly 10 ha in the centre of each plot and marked with surveyor's tape. One

mid-crown branch (20 cm length) from each quadrant of the selected tree was clipped with a pole pruner. The branches were pooled by plot, put in plastic bags and labeled. The bags were transported to the field laboratory in coolers kept at 0°C. In the field laboratory, the needles of the 1981 and 1982 growths from each pooled plot sample were clipped separately with clean scissors. Each sample was divided into two separate samples for duplicate analysis. The samples were mixed thoroughly and stored at -20°C in sealed plastic bags until analyzed.

Samples from Control Plot

A control site, similar in all aspects to the conifer forests of New Brunswick but one that has never been exposed to fenitrothion spray was selected in Searchmont, about 50 km north of Sault Ste. Marie, Ontario. All the necessary terrestrial and aquatic substrates were sampled from the plots selected in this site.

Analytical Procedures

Water: The two composite water samples *(ca* 1.5 L each) from each site were mixed with 100 ml of 20% aqueous sodium chloride and 500 mL aliquots were partitioned twice with 100 mL of pesticide grade dichloromethane. The pooled organic phase was dried through a column of anhydrous Na_2SO_4, flash-evaporated gently to dryness and the residues were taken up in ethyl acetate for gas-liquid chromatographic (GLC) analysis without any further cleanup.

Sediment, litter and soil: The sediment samples were filtered under suction to remove excess water. Ten gram aliquots of sediment, litter and soil samples in triplicate were separately extracted twice for 5 min with 100 mL of pesticide grade acetonitrile using Sorvall Omni-Mixers set at the maximum speed. The extracts were filtered quantitatively through Na_2SO_4 (heated overnight at 260°C prior to use) columns and concentrated under low pressure to about 60 mL. The concentrates were partitioned twice with 20 mL of pesticide grade hexane. The polar phases were flash-evaporated to dryness and the residues were dissolved in 10 mL of glass distilled or pesticide grade ethyl acetate so that 1 mL of extract was equivalent to 1 g of sample.

For column clean up, Pasteur pipets (Fisher Cat. No. 13-678-8) (14.5 cm x 0.8 cm i.d.) were packed from bottom to top with a glass wool plug, 3 cm of a 2:5 (w/w) mixture of acid-washed (Brown, 1975) Nuchar-activated charcoal (Kodak)/Whatman CF-11 cellulose and 1 cm of anhydrous Na_2SO_4. The packed columns were prewashed with 10 mL of ethyl acetate. One mL aliquots of the crude extracts equivalent to 1 g of the substrates were transferred quantitatively to the cleanup columns and eluted with 15 mL of ethyl acetate at the rate of 2 drops/sec. The resulting eluates were collected and concentrated in a flash evaporator at 30°C for GLC analysis.

Fir foliage, moss and water-cress: Prior to blending, the excess water present in thawed moss and water-cress samples was removed by pressing them in folds of absorbent paper. The plant tissues (triplicate of 10 g) were then mixed with 20 g of Na_2SO_4 and extracted twice with CH_3CN (100 mL) in a Sorvall Omni-Mixer and the extracts were cleaned up for GLC analysis as described in the previous section.

Fish: Each composite fish sample was chopped into small pieces with a sharp knife and mixed thoroughly. Ten gram aliquots in triplicate of cut up fish with 20 g of Na_2SO_4 and 100 mL of acetonitrile were homogenized in a Polytron (Type PT-20) for 3 min and the supernatant extract was filtered under suction through a column of Na_2SO_4. The residue was re-extracted with 100 ml of acetonitrile and filtered through the same Na_2SO_4 column. The column was rinsed with 20 mL of the solvent and the extracts were pooled and processed as described under sediment.

Air: The three composited toluene samples used to trap the airborne fenitrothion were

first dried by passing them through a column of Na_2SO_4, flash evaporated gently at low pressure to 1 mL and passed through the charcoal-cellulose column to adsorb the impurities. The insecticide was then eluted as described above with ethyl acetate and analysed by GLC.

GLC Analysis: Fenitrothion residues present in the final extracts were analyzed by the Tracor 550 gas chromatograph, fitted with an NP-FID (Tracor model 702) detector. A glass (Pyrex) column (1.2 m x 2 mm i.d.) packed with 1.5% OV-17 + 1.95% OV-210 on 80/100 mesh chromosorb W (H.P.) was used. Helium was the carrier gas at 45 mL/min. The operating parameters were as follows: detector temperature 250°C; inlet and outlet temperatures respectively 220°C and 230°C; column temperature 180°C; plasma flow rate 4.0 mL/min for hydrogen and 110 mL/min for air. The retention time for the insecticide under these conditions was 3.25 min.

Detector response was calibrated daily with analytical standard prepared in ethyl acetate. The cleaned extracts of each sample were injected thrice and the average peak height was calculated. Quantification of the samples was based on average peak heights of the external standard which was injected before and after the sample. Each value recorded in Tables 3 and 4 is the average of three measurements for each substrate from each plot along with the appropriate standard deviation (SD) found in them. Results are not corrected for extraction efficiency.

Samples of fir foliage, litter, soil, sediment, and fish samples from the control plot were fortified in three replicates with 1.0, 0.10 and 0.01 ppm (µg/g) levels of fenitrothion in ethyl acetate. Each substrate was extracted and analysed as per the method described above to evaluate the extraction efficiency. The fortification levels for water were the same except that they were in ppb (µg/L) units. The percent recovery levels are given in Table 2. Each mean percentage with its standard deviation was derived from three replicates. The minimum detection limit (MDL) for the insecticide was 0.01 ppm of wet or fresh weight of the substrates, for air 10 ng/m^3 and for water it was 0.01 ppb. None of the clean extracts of unfortified control samples equivalent to 10 g of substrates showed any positive response to GLC that interfered with fenitrothion.

Moisture contents of foliage, soil, litter, sediment, moss and water-cress samples were determined by drying two 10 g duplicates of each sample at 105°C for 16 h in a thermostatic oven (AOAC, 1955).

Table 2. Percent recovery of fenitrothion from some forestry substrates after fortification

	% recovery ± SD (n = 3)		
Substrate	1.0 ppm	0.10 ppm	0.01 ppm
fir foliage	96 ± 4	98 ± 5	96 ± 7
litter	98 ± 6	96 ± 3	94 ± 7
soil	101 ± 3	98 ± 6	95 ± 6
sediment	98 ± 4	103 ± 7	92 ± 3
moss	96 ± 6	91 ± 9	87 ± 8
fish	95 ± 6	101 ± 4	91 ± 4
	1.0 ppb	0.10 ppb	0.01 ppb
water	98 ± 3	102 ± 4	97 ± 2

RESULTS AND DISCUSSION

Contamination of study plot from spray drift

The amounts of fenitrothion found in various forestry substrates collected during the 1982 operational spray season (May/June) in New Brunswick from plots not directly treated with the chemical are given in Table 3. The residue data found in similar samples collected nearly a year later (May, 1983) from the same plots prior to any spray application in the province are given in Table 4. None of the data recorded here are corrected for extraction efficiency. The results from aquatic plants, sediment and terrestrial components are expressed in

Table 3. Average concentrations[1] of fenitrothion in some forestry substrates sampled from plots not treated directly with fenitrothion during the middle (May/June) of 1982 spray season in New Brunswick

Plot no. / Substrate	P1	P2	P3	P4	P5	P6	P7	P8
Air (ng/m^3)	74 ± 8	48 ± 11	82 ± 14	81 ± 7	64 ± 8	80 ± 4	62 ± 6	56 ± 3
Water (ppb) (stream)	0.01 ± 0.01	0.04 ± 0.02	0.07 ± 0.03	0.01 ± 0.01	0.02 ± 0.01	0.03 ± 0.02	0.02 ± 0.01	0.02 ± 0.01
(pond)	-	-	1.48 ± 0.08	-	0.71 ± 0.03	-	-	-
Water-cress (ppm)	-	-	-	-	-	-	-	0.18 ± 0.06 (0.84 ± 0.17)
Moss (ppm)	0.06 ± 0.02 (0.21 ± 0.09)	0.08 ± 0.03 (0.28 ± 0.08)	0.15 ± 0.04 (0.61 ± 0.11)	-	0.03 ± 0.01 (0.12 ± 0.04)	N.D.	N.D.	N.D.
Fish (ppm)	N.D.	-	-	-	-	-	N.D.	N.D.
Sediment (ppm) (stream)	N.D.	N.D.	0.11 ± 0.04 (0.15 ± 0.06)	N.D.	0.06 ± 0.03 (0.09 ± 0.05)	N.D.	0.08 ± 0.04 (0.12 ± 0.06)	0.15 ± 0.06 (0.21 ± 0.09)
(pond)	-	-	0.21 ± 0.05 (0.28 ± 0.07)	-	0.06 ± 0.02 (0.08 ± 0.03)	-	-	-
Fir foliage (ppm)								
1981 growth	0.38 ± 0.12 (0.71 ± 0.24)	0.49 ± 0.11 (0.81 ± 0.22)	0.62 ± 0.21 (0.98 ± 0.37)	0.43 ± 0.11 (0.80 ± 0.35)	0.33 ± 0.12 (0.61 ± 0.21)	1.06 ± 0.22 (2.07 ± 0.47)	0.50 ± 0.14 (0.79 ± 0.33)	0.41 ± 0.11 (0.69 ± 0.25)
1982 growth	0.36 ± 0.06 (0.72 ± 0.08)	0.53 ± 0.20 (0.98 ± 0.33)	0.66 ± 0.31 (1.08 ± 0.41)	0.47 ± 0.06 (0.82 ± 0.27)	0.39 ± 0.17 (0.66 ± 0.31)	1.12 ± 0.41 (2.18 ± 0.72)	0.64 ± 0.21 (0.98 ± 0.38)	0.42 ± 0.16 (0.79 ± 0.31)
Litter (ppm)	0.04 ± 0.01 (0.07 ± 0.03)	0.07 ± 0.03 (0.11 ± 0.06)	0.08 ± 0.02 (0.13 ± 0.06)	0.02 ± 0.01 (0.06 ± 0.04)	0.06 ± 0.03 (0.09 ± 0.04)	0.54 ± 0.13 (0.99 ± 0.27)	0.07 ± 0.03 (0.12 ± 0.04)	0.10 ± 0.04 (0.16 ± 0.07)
Soil (ppm)	0.08 ± 0.03 (0.11 ± 0.05)	0.03 ± 0.01 (0.05 ± 0.02)	0.06 ± 0.02 (0.09 ± 0.03)	0.01 ± 0.01 (0.02 ± 0.02)	0.12 ± 0.04 (0.18 ± 0.06)	0.20 ± 0.06 (0.29 ± 0.08)	0.10 ± 0.03 (0.16 ± 0.04)	0.09 ± 0.02 (0.13 ± 0.04)

[1] Minimum detection limit (MDL) for air 10 ng/m^3, for water 0.01 ppb and for all others 0.01 ppm.
Residue values without parentheses = residues in terms of wet weight.
Residue values with parentheses = residues in terms of oven-dry weight [105°C for 16 h in a thermostatic oven (AOAC, 1955)].

Table 4. Average concentrations[1] of fenitrothion in some forestry substrates sampled in May 1983 prior to any spray application from the same plots used during the 1982 study in New Brunswick

Plot no. / Substrate	P1	P2	P3	P4	P5	P6	P7	P8
Air (ng/m^3)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Water (ppb) (stream)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
(pond)	-	-	0.07 ± 0.05	-	0.06 ± 0.02	-	-	-
Water-cress (ppm)	-	-	-	-	-	-	-	N.D.
Moss (ppm)	N.D.	N.D.	N.D.	-	N.D.	N.D.	N.D.	N.D.
Fish (ppm)	N.D.	-	-	-	-	-	N.D.	N.D.
Sediment (ppm) (stream)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
(pond)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Fir foliage (ppm)								
1981 growth	0.45 ± 0.04 (0.75 ± 0.07)	0.56 ± 0.05 (1.00 ± 0.09)	0.45 ± 0.04 (0.79 ± 0.07)	0.62 ± 0.05 (1.11 ± 0.09)	0.39 ± 0.04 (0.71 ± 0.07)	1.16 ± 0.11 (2.10 ± 0.18)	0.52 ± 0.05 (0.91 ± 0.09)	0.32 ± 0.04 (0.55 ± 0.07)
1982 growth	0.58 ± 0.05 (0.99 ± 0.09)	0.63 ± 0.06 (1.10 ± 0.11)	0.42 ± 0.04 (0.69 ± 0.07)	0.80 ± 0.08 (1.32 ± 0.13)	0.15 ± 0.03 (0.27 ± 0.05)	0.67 ± 0.07 (1.17 ± 0.12)	1.00 ± 0.25 (1.73 ± 0.43)	0.12 ± 0.03 (0.23 ± 0.04)
Litter (ppm)	N.D.	0.02 ± 0.01 (0.05 ± 0.02)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Soil (ppm)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

[1] Minimum detection limit (MDL) for air 10 ng/m^3, for water 0.01 ppb and for all others 0.01 ppm.
Residue values without parentheses = residues in terms of wet weight.
Residue values with parentheses = residues in terms of oven-dry weight [105°C for 16 h in a thermostatic oven (AOAC, 1955)].

terms of "ppm (µg/g) fresh or wet weight" for ecological interpretation and "ppm oven-dry weight" in parentheses for more standardized comparison of residues between species. The concentration based on fresh or wet weight basis is used throughout the following discussion.

Comparison of the data in the two sampling periods clearly demonstrated the contamination of study plots during May/June of 1982 by spray drift from nearby operations. Except fish, nearly all the substrates sampled in the 1982 spray season contained measurable levels of fenitrothion. The average air concentration of the chemical during the entire 15 d sampling period in 1982 remained around 68 ± 8 ng/m^3 (range 48 to 82 ng/m^3), which confirmed that the contamination of the air masses and subsequent deposition on the substrates in plots P1 to P8 occurred continuously throughout the sampling period. The chemical may have entered the sample plots from any one of many possible directions (Fig. 1), depending on the meteorological conditions. The concentrations of fenitrothion in stream waters were usually low (mean 0.03 ppb, range 0.01 to 0.07 ppb) and were close to the detection limit (0.01 ppb) whereas in stagnant waters, the average concentration found was 1.10 ppb. The aquatic plants, moss and water-cress on average contained respectively 0.05 ppm and 0.18 ppm (wet weight). The stream sediments from all 8 plots on average contained 0.05 ppm (wet weight) compared to the 0.13 ppm found in pond sediments. Among the terrestrial components, the fir foliage (fresh wt) of 1981 and 1982 growths respectively contained on average 0.53 ppm (range 0.33 to 1.06 ppm) and 0.57 ppm (range 0.36 to 1.12 ppm) of fenitrothion compared to the litter and soil samples which contained much lower levels of 0.12 ppm (range 0.02 to 0.54 ppm) and 0.07 ppm (range 0.01 to 0.20 ppm) respectively. Contrary to these observed residue data, the samples collected from the same plots nearly a year later (May, 1983), prior to any spray application, did not contain measurable levels of fenitrothion in air, stream water, sediment, aquatic plants, fish and soil. Only the pond water samples from plots P3 and P5 and the litter sample in P2 contained detectable levels of fenitrothion but at much lower levels compared to the values observed a year earlier in 1982. Surprisingly, the average values found in the fir needles (fresh weight) of 1982 and 1983 growths were nearly the same *i.e.*, 0.56 ppm (range 0.32 to 1.16 ppm) for the 1982 and 0.55 ppm (range 0.12 to 1.00 ppm) for the 1983 growths.

The data presented here clearly demonstrate that the off-target fallout of fenitrothion during the sampling period contributed considerably to the residue levels found in most of the substrates analysed, agreeing with findings reported earlier by Pearce *et al.* (1979) and Sundaram (1984a). This being the case, it is advisable that in future, field testing of new chemicals for environmental chemistry, biological impact and efficacy should be conducted in areas sufficiently removed from any operational spray program to minimize possible ambiguity in the data generated.

Persistence of fenitrothion in forestry substrates

The results in Table 4 suggest that fenitrothion does not persist to detectable levels in most of the forestry substrates, agreeing with observations made earlier (Yule and Duffy, 1972; Sundaram, 1974a, b; Eidt and Sundaram, 1975; Miyamoto, 1977; Kingsbury, 1978; Morrison and Wells, 1981; Ayer *et al.*, 1984, Sundaram, 1984b). A short-term persistence of the chemical of a week or so in some aquatic flora and fauna has been reported (Kingsbury, 1976; Moody *et al.*, 1978; Morrison and Wells, 1981; Eidt *et al.*, 1984). There is also evidence in the literature (Yule, 1974; Sundaram, 1974b; McNeil *et al.*, 1979; Mallet and Volpé, 1982; Sundaram and Sundaram, 1982; Ayer *et al.*, 1984; Sundaram, 1984b) on the long-term persistence of fenitrothion in conifers. The data in Table 4 conclusively prove that fenitrothion persists in conifer needles for a year and beyond, at an average of about a 0.55 ppm (fresh weight) level, although the chemical is reported to have short life and instability in various crop plants (Miyamoto, 1978).

Table 5. Analysis of variance of fenitrothion residues in Fir foliage for (A) year growth of foliage and, (B) between plots of P1 to P8

Type of analysis	Source of analysis	DF	SS	MS	F-ratio
(A)	wet weight of 1982 and 1983 studies	3	0.0092	0.0031	0.04
	P1 - P8	28	1.9286	0.0689	
	Total	31	1.9378		
	oven dry weight of 1982 and 1983 studies	3	0.048	0.016	0.07
	P1 - P8	28	6.713	0.240	
	Total	31	6.762		
(B)	wet weight of 1982 and 1983 studies	7	1.3594	0.1942	8.06
	year growth of foliage	24	0.5784	0.0241	
	Total	31	1.9378		
	oven dry weight of 1982 and 1983 studies	7	4.865	0.695	8.79
	year growth of foliage	24	1.8966	0.079	
	Total	31	6.7616		

The fenitrothion concentrations (Tables 3 and 4) in a) fresh and b) dry weight samples of foliage and c) the residue levels found between the 1982 and 1983 growths (fresh and dry weights) were analyzed using the statistical procedures i) analysis of variance, ii) Duncan's Multiple Range Test and iii) the more widely used Student-Newman-Kuel's Test. Analysis of variance (Table 5) did not show any significant differences between the residues found in 1981 and 1982 growths, but some significant differences were noted in the data found among the plots P1 to P8. The Duncan's Test (Table 6) showed some significant differences in the residue levels found between the 1981 and 1982 growths as well as in the data between the plots. On the other hand the Student-Newman-Kuel's Test (Table 7) showed no significant differences in residue levels between the 1981 and 1982 growths but the data in plot P6 showed significant difference from other plots. Considering the low residue levels found in the plots, the small variation between the two growth regimes, and the lack of information on the spray histories of the plots, more emphasis should be given to the statistical conclusions arrived at with the Student-Newman-Kuel's test.

Conifer foliage is the primary receptor of fenitrothion during spray application. The mechanisms of dissipation are primarily volatilization, weathering action of humidity, photolysis, hydrolysis and to a lesser extent by enzymatic degradation (Sundaram and Sundaram, 1982; Sundaram, 1984b). Most of the sprayed fenitrothion (*ca* 90%) intercepted by conifer needles was lost rapidly within two weeks and the little that remained, being lipophilic, was probably absorbed, transported and stored in cuticular waxes of the foliage thus resisting leaching, volatilization, photo- and biodegradations. Polar resinous constituents of the cuticle (Kolattukudy, 1980) probably acted as solvents causing the fenitrothion molecules to permeate through cuticular pores. The lipoid nature of the cuticle

Table 6. Results of Duncan's multiple range test of the fenitrothion residue in foliage for the difference in (A) residues between year's growth foliage of 1981 and 1982, (B) residues between P1 to P8

Type of study	Samples	N	Mean*	Error MS
(A)	**1st-81-W	8	0.5275 a	0.1543
	2nd-82-W	8	0.5463 a b	
	2nd-81-W	8	0.5588 a b	
	1st-82-W	8	0.5738 a b	
	1st-81-O	8	0.9325 a b c	
	2nd-82-O	8	0.9375 a b c	
	2nd-81-O	8	0.9900 b c	
	1st-82-O	8	1.0263 c	
(B)	***P5	8	0.4388 a	0.1046
	P8	8	0.4412 a	
	P1	8	0.6175 a b	
	P3	8	0.7113 a b	
	P2	8	0.7625 a b	
	P4	8	0.7963 a b	
	P7	8	0.8838 b	
	P6	8	1.4413 c	

*Mean followed by the same letter not significantly different P = 0.05, df = 56.
**1^{st}: 1982 study; 2^{nd}: 1983 study; W: wet; O: ovendry.
***p = plot number.

allowed the passage of the insecticide molecules to the cutin layer for storage thus acting as a micro sink for the more persistent residues. The stored molecules were not translocated to other parts of the conifer tree (Prasad and Moody, 1976). At this juncture, since the spray histories of the plots are unknown, and there are no significant differences among the residue levels found in the needles of all the eight plots, it is impossible to demonstrate the accumulation pattern of the chemical with frequency of exposure.

In previous field trials (Yule and Duffy, 1972; Sundaram, 1974a, b; Sundaram *et al.*, 1983; Holmes *et al.*, 1984), a prolonged persistence of the chemical in natural waters and forest litter has never been observed. We can postulate that the low concentration levels found in the two pond water samples from plots P3 and P5 and the one litter sample from plot P2 (Table 4) could be due to leaf fall and foliar leaching of contaminated fir needles and twigs and surface run off during rain rather than due to persistence of the chemical in these two substrates.

The ecological significance of the low levels of fenitrothion (*ca* 0.55 ppm, wet weight) persisting in conifers for an extended period of time is not yet fully explored. McNeil *et al.* (1979) and Eidt and Mallet (1985) reported that such levels were toxic to the larvae of conifer sawflies. The continuing use of fenitrothion, would probably warrant a rigorous study to demonstrate the long term biological significance of the chemical to nontarget species which consume the contaminated fir needles and inhabit the conifer environment.

Table 7. Results of Student-Newman-Kuel's Multiple range test of the fenitrothion residue in foliage for the differences in (A) residues between years growth foliage of 1981 and 1982, (B) residues between P1 to P8

Type of study	Samples	N	Mean*	Error MS
(A)	**1st-81-W	8	0.5275 a	0.1543
	2nd-82-W	8	0.5463 a	
	2nd-81-W	8	0.5588 a	
	1st-82-W	8	0.5738 a	
	1st-81-O	8	0.9325 a	
	2nd-82-O	8	0.9375 a	
	2nd-81-O	8	0.9900 a	
	1st-82-O	8	1.0263 a	
(B)	***P5	8	0.4388 a	0.1046
	P8	8	0.4412 a	
	P1	8	0.6175 a	
	P3	8	0.7113 a	
	P2	8	0.7625 a	
	P4	8	0.7963 a	
	P7	8	0.8838 a	
	P6	8	1.4413 b	

* Mean followed by same letter not significantly different = 0.05; df = 56
** 1st: 1982 study; 2nd: 1983 study; W: wet; O: oven dry
*** P: plot number

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